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| EXAMINER |
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WONG, EDNA

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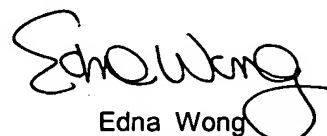
Commissioner for Patents

The prior art made of record and relied upon, SU 1544847, has been translated into English. The English translation is submitted herewith.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Edna Wong whose telephone number is (571) 272-1349. The examiner can normally be reached on Mon-Fri 7:30 am to 4:00 pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Nam Nguyen can be reached on (571) 272-1342. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.


Edna Wong
Primary Examiner
Art Unit: 1753

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USSR Inventor's Certificate No.
SU 1544847 A1

A COMPLEX ADDITIVE FOR ACID ELECTROLYTES FOR THE PRODUCTION OF
COMPOSITE COATINGS BASED ON NICKEL AND A NICKEL-COBALT ALLOY

Ramanauskene et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. SEPTEMBER 2006
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UNION OF SOVIET SOCIALIST REPUBLICS

USSR State Committee

On Matter of Inventions and Discoveries

DESCRIPTION OF INVENTION

For Inventor's Certificate of SU 1544847 A1

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|-------------------------|--------------------------------------|
| Int. Cl. ⁵ : | C 25 D 15/00 |
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A COMPLEX ADDITIVE FOR ACID ELECTROLYTES FOR THE PRODUCTION OF
COMPOSITE COATINGS BASED ON NICKEL AND A NICKEL-COBALT ALLOY

[Komplóksnaya dobavka v kislýe elektrolity dlya polúchenia kompozitsionnykh pokrytii na
osnove nikelya i splava nikel'-kobal't]

| | |
|-------------|--|
| Inventors: | D.-B. K. Ramanauskene, et al. |
| Applicant: | Institute of Chemistry and Chemical Technology, Academy of Sciences of the Lithuanian SSR |
| References: | 1. USSR Inventor's Certificate 478873, Cl. C 25 D 3/18, 1972. 2. FRG Patent No. 3313871, Cl. C 25 D 15/00, 1984 |

The invention relates to electroplating, specifically to the deposition of composite electrochemical coatings, and can be used in the automobile, tool, machine construction and other branches of industry where hard and wear-resistant protective/decorative coatings are required.

The goal of the invention is an improvement of the hardness of the composite coatings.

The coating is obtained in electrolytes that contain a complex additive in the form of methyl cellulose and betaine 2-(4-pyridyl)ethanesulfonic acid. The composite electrochemical coating (CEC) is produced at a current density of 5-8 A/dm² and a temperature of 45-50.

The combined use of betaine 2-(4-pyridyl)ethanesulfonic acid and methylcellulose contributes to better quality of CECs with high microhardness (700-850 kg/mm²) and high content of non-metallic micropowders (6-20 vol%), including limiting concentrations of the additives. The additive produces a dual effect: not only is the microhardness of the CEC increased and the coprecipitation of powders with the metal promoted, but the production of high quality thick coatings is furthered. It modifies the surface properties of the powder and affects the granularity of the structure of the metal and therefore hard coating with powder concentration are obtained. The additive even increases the powder to sedimentation in the electrolyte.

Example 1

20.92 g 2-(4-pyridyl)ethanesulfonic acid and 4-g sodium hydroxide are dissolved in 100 mL water, 8.04 g ethylene chlorohydrin is added, and the mixture is boiled with reflux for 16 h. Then the solution is concentrated in a vacuum, the dry residue is dissolved in 100 mL cold concentrated HCl. The undissolved sodium chloride is filtered out through a glass filter, and the filtrate is vacuum concentrated. The residue is recrystallized from a mixture of ethanol and water (3:1). The result is 18.77 g of product, yield 81.2%, m.p. ~218°C (dec.).

Calculated, %: C 46.74; h 5.66; S 13.89.

C₉H₁₃NO₄S.

Found, %: C 46.89; 46.74; h 5.66; 4.83; S 13.89; 13.66.

Example 2

12.13 g product, yield 92.9%, is obtained analogously from 10.46 g 2-(4-pyridyl)ethanesulfonic acid, 2 g sodium hydroxide in 50 mL water with 5.52 g glycerol α -monochlorohydrin, and is recrystallized from a mixture of methanol and water (2:1); m.p. ~239°C (dec.).

Calculated, %: C 45.96; h 5.78; S 12.27.

C₁₀H₁₅NO₅S.

Found, wt%: C 45.63; 45.60; h 5.88; 5.71; S 13.02; 11.69.

Example 3

3.6 g acrylic acid and 0.1 mL triethanolamine are added to a solution of 9.36 g 2-(4-pyridyl)ethanesulfonic acid in 50 mL water. The resulting reaction mixture is boiled for 16 h,

then vacuum evaporated. The residue is recrystallized from methyl alcohol. The result is 9.9 g product, yield 76.4%, m.p. $\sim 254^{\circ}\text{C}$ (dec.).

Calculated, %: C 46.32; H 5.05; S 12.36.

$\text{C}_{10}\text{H}_{13}\text{NO}_5\text{S}$

Found, %: C 46.03; 46.37; H 5.12; 5.03; S 12.03; 12.45.

Example 4

10.46 g 2-(4-pyridyl)ethanesulfonic acid sodium salt is dissolved in 50 mL water, a few drops of an alcohol solution of phenolphthalein and 4.63 g epichlorohydrin are added. The mixture is vigorously stirred at room temperature and upon the appearance of a red-violet color dilute ($\sim 2\text{N}$) hydrochloric acid is gradually added. The acid is added at a rate so that the reaction mixture does not become intensive colored. When the reaction slows, the temperature is raised to $40\text{--}50^{\circ}\text{C}$. After the end of the reaction 7.46 g triethanolamine is added and the mixture is boiled at reflux for 16 h. Then the water is evaporated until the solution is dry, using a rotary evaporator, and the residue is extracted with boiling ethyl alcohol (3x200 mL). The crystals that form upon cooling are filtered out and dried in a vacuum dryer. The result is 15.75 g, yield 73.4%, and is recrystallized from ethyl alcohol.

Calculated, %: N 6.53.

$\text{C}_{16}\text{H}_{29}\text{ClN}_2\text{O}_7\text{S}$.

Found, %: N 6.92, 7.10.

The structure of the synthesized compounds was confirmed by means of the IR and UV spectra. Methyl cellulose is industrially manufactured. The additive is introduced into the electrolyte in the follow way.

First, a sulfuric or sulfamic acid electrolyte for a nickel plating or an electrolyte for deposition of an Ni-Co alloy of known composition (examples are given in the table) is prepared. It is purified with activated carbon and selective purification. In separate container the required amount of the micropowder is weighted out and mixed with a small quantity of the purified electrolyte. The required amount of a solution of methyl cellulose and betaine 2-(4-pyridyl)ethanesulfonic acid is added to the resulting porridge-like mass, thoroughly mixed, and after a 20 minute wait the resulting mixture is transferred to a bath containing the necessary amount of electrolyte. The electrolyte and suspension are mixed with compressed air.

Industrial micropowders used are: green silicon carbide ("KZ") with dispersity M5 (basic fraction $3\text{--}5\text{ }\mu\text{m}$), white electrocorundum "EB" M3 (basic fraction $1\text{--}3\text{ }\mu\text{m}$), electrocorundum M10, boron nitride β (Elbor) M3. The particle sizes of the micropowder that is used should not exceed $20\text{ }\mu\text{m}$, and its concentration in the electrolyte can be $50\text{--}300\text{ g/L}$.

Specific examples illustrating the use of the additive are given in the table.

As can be seen from the table, the additive has the possibility of producing CECs with various nonmetallic micropowders: carbides, oxides, nitrides and boron. The additive can be used to produce self-lubricating composite coatings. For example, high quality coatings 12 vol% inclusions are obtained with a graphite micropowder.

Analysis of the examples shows that the concentration of betaine to 2-(4-pyridyl)ethanesulfonic acid can be increased up to 1.5 g/L (Example 12) without sacrifice in the quality of the resulting CEC. The coatings that are obtained have a high percentage of inclusions and high microhardness (20.8 vol% and 890 kg/cm², respectively). However, an increase of the concentration of the additive above the said limit can lead to cracking of the CEC. The maximum methyl cellulose concentration is limited by the fact that high quantities of it have an adverse effect on the coprecipitation of the powder (Example 11), although a very stable suspension is formed.

If betaine 2-(4-pyridyl)ethanesulfonic acid is added in an amount less than 0.25 g/L the resulting CECs have a microhardness that is not very high. Thus, to obtain hard CECs the concentration of the additive must be maintained in the range of 0.3-1.2 g/L. The broad interval of working concentrations for the additive is an important property of the electrolyte when producing thick coatings.

Claim

A complex additive for acid electrolytes for the production of composite coatings based on nickel and a nickel-cobalt alloy, which contains a nitrogen-containing heterocyclic compound, which is distinguished by the fact that, with the goal of increasing the hardness of the coatings, it additionally contains methyl cellulose and it contains as the nitrogen-containing heterocyclic compound betaine 2-(4-pyridyl)ethanesulfonic acid of the general formula



where R₁ is h or OH;

R₂ is OH₁-CH₂OH,

-COOH₁-CH₂N⁺(CH₂CH₂O₃)₃Cl,

in the following ratio of components, g/L:

| | |
|--|----------|
| Methyl cellulose | 0.15-2.0 |
| Betaine 2-(4-pyridyl)ethanesulfonic acid | 0.3-1.5 |

| 1 | 2 | | | | | | | | | | | | |
|--|-------------|------|------|------|-----|------|------|------|------|------|-----|------|-----|
| | Пример | | | | | | | | | | | | |
| Состав электролита, г/л, режим осаждения и свойства ЦП | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| (Базовый) | (Известный) | | | | | | | | | | | | |
| Сернистый никель (гидрат) | 300 | 300 | 300 | 300 | 240 | 240 | 300 | 300 | 240 | 400 | 300 | 320 | 320 |
| Сульфаминиоокисный никель | - | - | - | - | - | - | - | - | - | 400 | - | - | - |
| Хлористый никель (гидрат) | 45 | 45 | 45 | 45 | 45 | 45 | 40 | 40 | 40 | 25 | 45 | 45 | 40 |
| Сернистый кобальт (гидрат) | - | - | - | - | - | - | - | -25 | - | - | - | - | - |
| Вольная кислота | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 40 | 40 | 40 | 40 |
| Карбид вранья КЗ КЗ | 100 | 100 | 100 | 150 | - | - | - | - | 100 | - | 200 | 300 | 150 |
| Электрокорунд 36 М10 | - | - | - | - | - | - | 100 | - | - | - | - | - | - |
| Электрокорунд 36 КЗ | - | - | - | - | - | - | - | - | 100 | - | - | - | - |
| Нитрид бора В (16 мкм) | - | - | - | - | 75 | - | - | - | - | - | - | - | - |
| Эльбор КЗ | - | - | - | - | - | 30 | - | - | - | - | - | - | - |
| Аморфный бор | - | - | - | - | - | - | - | 30 | - | - | - | - | - |
| Метилсиль флюидовый | - | 0,2 | - | - | - | - | - | - | - | - | - | - | - |
| Вещи 2-(4-пиримидил)-этансульфонаты | - | - | 0,4 | 0,8 | 0,6 | 0,5 | 0,5 | 0,3 | 0,6 | 1,0 | 0,7 | 1,5 | 0,6 |
| Метилцеллюлоза | - | - | 0,3 | 0,4 | 1,2 | 0,5 | 0,15 | 0,4 | 0,8 | 0,6 | 1,5 | 0,5 | 2,0 |
| Вязкость электролита, А/дм ² | 5 | 5 | 5 | 6 | 7 | 4 | 5 | 7 | 8 | 7 | 5 | 5 | 5 |
| pH электролита | 4 | 5 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 3,6 | 3,6 | 4 |
| Температура электролита, °С | 45 | 45 | 45 | 45 | 45 | 50 | 50 | 50 | 45 | 50 | 45 | 45 | 45 |
| Толщина покрытия, мкм | 50 | 50 | 50 | 150 | 50 | 50 | 250 | 50 | 50 | 50 | 50 | 100 | 50 |
| Содержание включений микропорошка, об. % | 1,5 | 13,2 | 15,0 | 12,7 | 6,3 | 10,5 | 13,7 | 16,0 | 13,0 | 13,5 | 2,8 | 20,8 | 4,5 |

| 1 | 2 | | | | | | | | | | | | |
|--|-------------|------|------|------|------|------|------|-----|------|-----|-----|------|------|
| | Пример | | | | | | | | | | | | |
| Состав электролита, г/л, режим осаждения и свойства ЦП | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| (Базовый) | (Известный) | | | | | | | | | | | | |
| Нитрогенность, мг/см ² | 280 | 630 | 370 | 725 | 580 | 800 | 780 | 490 | 700 | 690 | 680 | 890 | 690 |
| Устойчивость суспензии (время седиментации 3 см), мин | 16 | 9 | 21 | 41 | 13 | 31 | 19 | 16 | 30 | 125 | 350 | 127 | 250 |
| Внутреннее напряжение, мг/см ² | 790 | 1620 | 1160 | 1040 | 1125 | 1200 | 1050 | 660 | 1150 | 450 | 980 | 1520 | 1400 |
| Пластичность, % | 4,2 | 31 | 4,3 | 7,7 | 7,7 | 12 | 4,2 | 2,4 | 4,2 | 4,2 | 7,1 | 2,4 | 2,5 |

7. При этом в нем: выход по току во всех случаях составляет 94-98%; скорость осаждения при 5 А/дм² порядка 1 мкм/мин; рассеиваемая плотность на металле Херифга-Аллен 24-26%; покрытия могут достигать толщиной 1000 мкм и более.

- Key: 1 Composition of electrolyte, g/L
 Precipitation conditions and properties of CEC
 2 Example
 3 (Base)
 4 (Known)
 5 Nickel sulfate (hydrate)
 Nickel sulfamate
 4. Nickel chlorite (hydrate)
 Cobalt (hydrate)
 Sulfuric acid
 Silicon carbide KZ, M5

Electrocorundum EB, M10

Electrocorundum EB, M3

Boron nitride (14 μm)

Elbor M3

Amorphous boron

Methyl violet

Betaine 2-(4-pyridyl)ethanesulfonic acid

Methyl cellulose

Cathode current density, A/dm^2

pH of electrolyte

Electrolyte temperature, $^{\circ}\text{C}$

Thickness of coating, μm

Concentration of micropowder inclusions, vol%

6 Microhardness, kg/mm^2

Stability of suspension (3 cm sedimentation time), min

Internal stresses, kg/cm^2

Plasticity, %

7 Note: Current efficiency in all cases 94-98%; sedimentation rate 3 A/dm^2 on the order of 1 $\mu\text{m}/\text{min}$; throwing power determined by the Haring-Blum method 24-26%; coating can be applied in a thickness of 1000 μm and greater.